

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference PV/292/PCT	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/CZ 00/ 00067	International filing date (day/month/year) 11/09/2000	(Earliest) Priority Date (day/month/year) 17/09/1999
Applicant SELLIER & BELLLOT, A.S.; et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/CZ 00/00067

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 - C06C7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C06C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 167 736 A (G.C. MEI ET AL.) 1 December 1992 (1992-12-01) claims ---	1-7
Y	US 5 216 199 A (R.K. BJERKE ET AL.) 1 June 1993 (1993-06-01) claims ---	1-7
A	US 5 547 528 A (J.A. ERICKSON ET AL.) 20 August 1996 (1996-08-20) column 2, line 34 - line 39 column 3, line 47 - line 59; claims 20-25 ---	1-7
A	FR 2 021 662 A (DYNAMIT NOBEL AKTIENGESSELLSCHAFT) 24 July 1970 (1970-07-24) claims --- -/--	1-7



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

28 December 2000

Date of mailing of the international search report

05/01/2001

Name and mailing address of the ISA

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Schut, R

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/CZ 00/00067

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 12 43 067 B (INDUSTRIE-WERKE KARLSRUHE AKTIENGESELLSCHAFT) claims ----	3
A	US 5 567 252 A (G.C. MEI ET AL.) 22 October 1996 (1996-10-22) claims -----	1-7

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CZ 00/00067

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5167736 A	01-12-1992	AT 162167 T	15-01-1998
		AU 662770 B	14-09-1995
		AU 2907592 A	07-06-1993
		BG 61604 B	30-01-1998
		BG 98746 A	31-05-1995
		BR 9206708 A	24-10-1995
		CA 2122710 A	13-05-1993
		CZ 9401100 A	15-12-1994
		DE 69224081 D	19-02-1998
		DE 69224081 T	13-08-1998
		DK 660812 T	09-02-1998
		EP 0660812 A	05-07-1995
		ES 2111084 T	01-03-1998
		FI 942051 A	04-05-1994
		HK 1008424 A	07-05-1999
		HU 68124 A, B	29-05-1995
		JP 7500562 T	19-01-1995
		KR 242749 B	01-02-2000
		NO 941631 A	03-05-1994
		RO 112423 B	30-09-1997
		RU 2127238 C	10-03-1999
		SK 51094 A	09-11-1994
		WO 9309073 A	13-05-1993
US 5216199 A	01-06-1993	AT 161943 T	15-01-1998
		BR 9202626 A	16-03-1993
		CA 2067302 A	09-01-1993
		DE 69223881 D	12-02-1998
		DE 69223881 T	16-04-1998
		DK 529230 T	27-04-1998
		EP 0529230 A	03-03-1993
		ES 2111586 T	16-03-1998
		GR 3025843 T	30-04-1998
		MX 9203997 A	01-01-1993
US 5547528 A	20-08-1996	ZA 9202779 A	30-12-1992
		AU 7103296 A	18-12-1996
		CA 2222065 A	05-12-1996
		EP 0828698 A	18-03-1998
		NO 975389 A	22-01-1998
FR 2021662 A	24-07-1970	WO 9638397 A	05-12-1996
		DE 1805358 A	18-06-1970
		BE 740680 A	01-04-1970
		CH 536798 A	15-05-1973
		GB 1284912 A	09-08-1972
		NL 6915133 A	28-04-1970
		NO 121321 B	08-02-1971
DE 1243067 B		NONE	
US 5567252 A	22-10-1996	NONE	

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PATENT COOPERATION TREATY

Rott, Růžicka & Guttman
Došlo dne
21.11.2001
Pořadové číslo 3429

PCT

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

JIROTKOVA, Ivana
ROTT, RUZICKA & GUTTMANN
P.O. Box 71
142 00 Praha 4
REPUBLIQUE TCHEQUE

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year) 14.11.2001

Applicant's or agent's file reference
PV/292/PCT

IMPORTANT NOTIFICATION

International application No.
PCT/CZ00/00067

International filing date (day/month/year)
11/09/2000

Priority date (day/month/year)
17/09/1999

Applicant
SELLIER & BELLOT, A.S.; et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office
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Tel. +49 89 2399 - 0 Tx: 523656 epmu d
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Koutsoftas, P

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PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PV/292/PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/CZ00/00067	International filing date (day/month/year) 11/09/2000	Priority date (day/month/year) 17/09/1999
International Patent Classification (IPC) or national classification and IPC C06C7/00		
Applicant SELLIER & BELLOT, A.S.; et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 3 sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the report</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input type="checkbox"/> Certain defects in the international application</p> <p>VIII <input checked="" type="checkbox"/> Certain observations on the international application</p>		
Date of submission of the demand 05/04/2001	Date of completion of this report 14.11.2001	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Werner, H Telephone No. +49 89 2399 8571 	

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/CZ00/00067

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

2-10 as originally filed

1,1a as received on 18/10/2001 with letter of 18/10/2001

Claims, No.:

6,7 as originally filed

1-5 as received on 18/10/2001 with letter of 18/10/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/CZ00/00067

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1-7
	No: Claims
Inventive step (IS)	Yes: Claims 1-7
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-7
	No: Claims

2. Citations and explanations
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

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SECTION V

1. Novelty and inventive step (Art 33(2) and (3) PCT.)

1.1. The present application fulfils the requirements for novelty and inventive step.

The present application claims a non-toxic and non-corrosive ignition mixture free of the commonly used diazodinitrophenol ("dinol"), a substance suspected to be carcinogenic. The ignition mixture comprises nitroesters or nitramines as fuel, tetrazene or a tetrazole derivatives as sensitizer, oxidizing agents, amorphous boron and a friction agent.

1.2. Documents cited in the international search report:

US-A-5 167 736, US-A-5 216 199, US-A-5 547 528 and US-A-5 567 252 disclose ignition mixtures comprising diazodinitrophenol.

FR-A-2 021 662 discloses ignition compound comprising a diazo derivate. The compound does not contain any boron.

DE 12 43 067 B discloses a primer composition comprising toxic heavy metals such as lead or barium.

1.3. The presently claimed composition and its improvements could not have been predicted and justify inventivity.

SECTION VIII

2. Clarity (Art. 64 PCT).

2.1. The embodiment of the invention described on pages 2 and 5 ("boron") does not fall within the scope of the claims ("amorphous boron"). This inconsistency between the claims and the description leads to doubt concerning the matter for which protection is sought, thereby rendering the claims unclear (Article 6 PCT).

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(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number
WO 01/21558 A1

- (51) International Patent Classification⁷: C06C 7/00 (74) Agent: JIROTKOVÁ, Ivana; Rott, Ruzicka & Guttman, P.O. Box 71, 142 00 Praha 4 (CZ).
- (21) International Application Number: PCT/CZ00/00067
- (22) International Filing Date:
11 September 2000 (11.09.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
PV 1999-3305 17 September 1999 (17.09.1999) CZ
- (71) Applicant (for all designated States except US): SEL-
LIER & BELLOT, A.S. [CZ/CZ]; Lidická 667, 258 13
Vlašim (CZ).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): NESVEDA, Jiří [CZ/CZ]; Havličkova 1596, 258 01 Vlašim (CZ). BRAN-
DEJS, Stanislav [CZ/CZ]; Zámecká 1490, 258 01 Vlašim (CZ). JIRÁSEK, Karel [CZ/CZ]; 258 01 Kondrac 85 (CZ).
- Published:
— With international search report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/21558 A1

(54) Title: NON-TOXIC AND NON-CORROSIVE IGNITION MIXTURE

(57) Abstract: A non-toxic and non-corrosive ignition mixture is created by combining the energy system and the pyrotechnic system. The energy system comprises a high explosive from the groups of nitroesters and nitramines and a sensibiliser of the type of tetrazene or derivatives of tetrazoles for its activation. The pyrotechnic system comprises an oxidizing agent from the group of oxides and peroxides of metals, from the group of salts of inorganic oxygen-containing acids, and a fuel which is amorphous boron. The mixture is supplemented with a friction agent which is preferably ground glass. Nitrocellulose, polyvinyl alcohol and acacia gum are used as bonding agents. Mixtures are utilizable in the field of ammunition production for the production of primers, especially for central ignition cartridges.

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Non-toxic and non-corrosive ignition mixture

Technical field

The invention concerns the field of ammunition production, especially the production of ignition mixtures for hunting and sports ammunition.

Background Art

All sorts of known ignition mixtures, which are presently used, i.e. both already dated mixtures based on mercuric fulminate, calcium chlorate and antimony sulphide, and newer non-corrosive mixtures based on tetrazene, lead trinitroresorcinate, lead dioxide, calcium silicide and antimony sulphide, emit during discharge a large amount of toxic heavy metals and they do not meet the environmental standards. That is why an extensive research has been carried out in the last ten years with an aim to develop a mixture that would not contain compounds of heavy metals such as lead, barium, mercury, antimony, and, at the same time, would retain non-corrosive properties of triscinate mixtures. The result is a mixture in which an aromatic diazo compound without metal content – dinol - fulfils the function of a primary explosive and tetrazene remains as a sensibilizer. The pyrotechnic system is in this case composed of a new oxidizing agent, zinc peroxide and titanium powder. The mixture can contain also other components such as friction agents, typically ground glass, and active propellants such as various sorts of nitrocellulose and nitroglycerine powders. Mixtures based on dinol are also known in which basically only the pyrotechnic system is modified. Oxidizing agents used include various oxides of metals – potassium nitrate, strontium nitrate, basic nitrates of copper and copper-ammonium nitrate and tin compounds. Neither these mixtures are a final solution. The basic problem here is the primary explosive itself – dinol. It is a carcinogenic compound with very unpleasant physiological effects. That is why there have been noted attempts to avoid dinol completely. EP 0656332 A1, in which the mixture is based only on pyrotechnic system and does not contain any explosive, offers one such solution. Here, the propellant is a hyperactive zircon powder, the oxidizing agent is a mixture of potassium nitrate and manganese dioxide, and the energy component is penthrithite.

-2-

There is no doubt that this mixture is according to the data of the inventors fully functional even though here a serious problem can also arise. It can be zircon itself. As the inventors themselves state, the active form of zircon is ignited by the influence of minute energy impulse both mechanically and thermally. It is well known that highly active metal powders, especially zircon, are pyrophoric and extremely reactive. They react both with air oxygen creating oxides and with air nitrogen creating nitrides and also with humidity creating hydrides. During transportation and storage, they have to be stored under water and during the production of mixtures water must be displaced using a water-immiscible organic solvent. According to the inventors, isopropyl alcohol is the most advantageous. The technology is then based on classical embroccating of pasty mixture into primer caps, however with the difference that the bonding agent is not an aqueous solution of the given organic compound but a solution of aerosil in isopropyl alcohol. During the production and the feeding of such mixtures, serious problems can arise such as handling extremely reactive zircon and moreover also technological problems resulting from the use of large amounts of organic solvents during the production.

Disclosure of the Invention

The above drawbacks are solved and totally removed by a non-toxic and non-corrosive ignition mixture the essence of which lies in that in the energy system, the primary explosive of the dinol type is replaced by a high explosive, which is activated by a sensitizer of the tetrazene type or by salts and derivatives of tetrazoles. Nitroesters such as penthrite and hexanitromanite but also nitrocellulose in the form of granulate and also nitroamines such as hexogene, octogene and tetryle, can be used as the high explosive. In order to increase the ignition power, the mixture must be supplemented with an appropriate pyrotechnic system. Mixtures with powder boron turned out to be the most suitable, especially those with brown, so-called amorphous, boron with large specific surface which in the case of commonly available specimens reaches 5 to 25 m²/g. Extensive testing has proven that amorphous boron is an excellent fuel and that it is able to create a perfect redox-system with any metal oxide, independent of valence, further with metal peroxides and all known salts of inorganic oxygen-containing acids.

Into the pyrotechnic system with boron, oxidizing agents can be selected from the group of compounds such as oxides of univalent metals: cuprous (I) - Cu₂O, bivalent: cupric (II) -

-3-

CuO, zinc (II) - ZnO, oxides of multivalent metals: bismuth (III) – Bi_2O_3 , bismuth (IV) – BiO_2 and bismuth (V) – Bi_2O_5 , ferric (III) – Fe_2O_3 , manganese (IV) – MnO_2 , stannic (IV) – SnO_2 , vanadic (V) – V_2O_5 and molybdenum (VI) – MoO_3 , peroxides of zinc – ZnO_2 and calcium – CaO_2 , saltpetre – KNO_3 and some special salts such as basic bismuth nitrates – $4\text{BiNO}_3(\text{OH})_2 \cdot \text{BiO}(\text{OH})$ and $\text{BiONO}_3 \cdot \text{H}_2\text{O}$, basic copper nitrate – $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$, diammo-copper nitrate – $\text{Cu}(\text{NH}_3)_2(\text{NO}_3)_2$, basic tin nitrate – $\text{Sn}_2\text{O}(\text{NO}_3)_2$. Boron creates the fastest burning system with compounds of bismuth. Systems with the highest heating effect originate when potassium nitrate, cupric oxide, ferric oxide and manganese oxide are used. The products of combustion can be both low-melting boron (III) oxide – B_2O_3 and volatile boron (II) oxide – BO which is more stable at higher temperatures, possibly also boron nitride – BN. The presence of these compounds in the products of combustion is very desirable from the viewpoint of perfect ignition of powder cartridge charges. In spite of its extraordinary reactivity, boron is chemically stable and it is not dangerous for handling. The expenses related to boron are compensated by its minimal content in stoichiometric mixtures, which does not exceed 20 weight percent. In order to increase sensitivity to strike by a blow, it is necessary to supplement the mixture with an appropriate friction agent, which is ground glass.

Considering that ignition mixtures produced in this way are in a very fine form it seems that the most suitable technology is handling when wet and, therefore, the mixture can also contain a certain amount of a water-soluble bonding agent. Commonly known bonding agents such as acacia gum, dextrin, polyvinyl alcohol, carboxymethyl cellulose and others are the most suitable. Should it be necessary to handle the mixture when dry, it would need to be granulated first. Granulation can be done both by using the above-mentioned bonding agents in water solutions or by using bonding agents soluble in organic solvents, e.g. nitrocellulose in acetone. The pyrotechnic system can be also grained after pressing and the grained product can be later used in the mixtures. In this case, the mixture does not have to contain any bonding agent because it can be easily fed when dry.

Within several years extensive tests have been performed both with primer caps filled with mixtures of the invention and with ammunition equipped with these primer caps.

The results of said functional tests show that it is possible, by a suitably chosen combination of the energy and pyrotechnic systems, to achieve desired characteristics of the mixture for a particular type of the primer. For example, for the smallest types of primer caps having the shortest reaction times, destined for the pistol and revolver ammunitions, it is necessary that

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the energy and pyrotechnic systems show as high reactivity as possible and have a high energy content at the same time. Primers showing the highest reactivity include nitro esters, which can be most easily initiated, among them mainly mannite hexanitrate, which is however predestined for special use due to its high cost and somewhat lower chemical stability. On the other hand, penthrite has shown itself as an ideal explosive with a wide range of utility. Similarly, nitrocellulose is a universal and multipurpose explosive, which can play roles of the combustible, the propellant and the binder at the same time. Nitramines are at a lower level in terms of effect than nitro esters and their initiability is lower. This renders them useful in primer caps having larger dimensions and longer reaction times, wherein they can be applied better than nitro esters, the very high effect of which could even be disadvantageous in some cases.

For comparison, results are presented of measurements of the primer caps 4.4/0.4 BOXER, destined for cartridges 9 mm LUGER, by the method DROP-TEST, in which we obtained a graphical function of the pressure values in dependence on the reaction time of the primer. The mixture of Example 20 was compared to a classical mixture based on lead trinitroresorcinate, the charge of which in the primer cap is by about 20 % higher. For both mixtures, identical values were obtained for maximal pressures - 100 bars – and reaction times – 100 microseconds.

Parameters of inner ballistics of the cartridge 9 mm LUGER with the primer cap filled with the above-described mixture were also measured. When a suitably chosen powder is used, it is possible, for a bullet weighing 7.5 g, to achieve muzzle velocities about 420 m/s without exceeding admissible values of maximal pressures in the chamber. Besides, functional shootings from various types of short and automatic weapons were performed, wherein the inventive ammunition showed reliable functioning.

It has been found that the mixtures of the invention, which contain tetrazene as the main explosive, show extraordinary handling safety. During burning of this mixture no development has been observed of any toxic combustion gases or compounds able to cause corrosion of the weapon.

Ignition mixtures created by combination of energy and pyrotechnic systems according to the mentioned essence of the invention are expressed by the following scheme:

data are presented in weight percentages

- high explosive 5 to 40 %

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- sensibilizer	5 to 40 %
- oxidizing agent	5 to 50 %
- boron	1 to 20 %
- friction agent	5 to 30 %
- possible bonding agent	0.1 to 5 %

Examples

The make is presented in weight percentages.

Example 1 – mixture without a bonding agent, suitable for handling when dry

tetrazene	25 %
penthrite	25 %
$4\text{BiNO}_3(\text{OH})_2 \cdot \text{BiO}(\text{OH})$	36.4 %
B	3.6 %
ground glass	10 %

Example 2 – similar mixture with higher sensitivity

a) dry variant – without bonding agent	b) wet variant
tetrazene	tetrazene
35 %	35 %
penthrite	penthrite
05 %	05 %
$4\text{BiNO}_3(\text{OH})_2 \cdot \text{BiO}(\text{OH})$	$4\text{BiNO}_3(\text{OH})_2 \cdot \text{BiO}(\text{OH})$
18 %	18 %
B	B
2 %	2 %
glass	acacia gum
10 %	0.5 %
	glass
	19.5 %

Example 3 – similar mixture

a) dry variant	b) wet variant
tetrazene	tetrazene
25 %	25 %
penthrite	tetryle
25 %	25 %
$\text{BiONO}_3 \cdot \text{H}_2\text{O}$	$\text{BiONO}_3 \cdot \text{H}_2\text{O}$
34 %	34 %
B	B
5.5 %	5.5 %
glass	acacia gum
10 %	0.5 %

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nitrocellulose	0.5 %	glass	10 %
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Example 4 – mixture with higher heating effect

a) dry variant – without bonding agent

tetrazene	35 %
penthrite	15 %
CuO	34 %
B	6 %
glass	10 %

b) wet variant

tetrazene	25 %
penthrite	25 %
CuO	34 %
B	5.5 %
polyvinyl alcohol	0.5 %
glass	10 %

Example 5

a) dry variant

tetrazene	35 %
penthrite	15 %
Bi ₂ O ₃	36 %
B	3.5 %
nitrocellulose	0.5 %
glass	10 %

b) wet variant

tetrazene	25 %
hexogene	25 %
Bi ₂ O ₃	36 %
B	3.5 %
polyvinyl alcohol	0.5 %
glass	10 %

Example 6

a) dry variant

tetrazene	35 %
penthrite	15 %
MnO ₂	31.5 %
B	8 %
nitrocellulose	0.5 %
glass	10 %

b) wet variant

tetrazene	25 %
tetryle	25 %
MnO ₂	31.5 %
B	8 %
acacia gum	0.5 %
glass	10 %

Example 7

a) dry variant

tetrazene	25 %
penthrite	25 %

b) wet variant

tetrazene	25 %
penthrite	25 %

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ZnO	34 %
B	5.5 %
nitrocellulose	0.5 %
glass	10 %

ZnO	34 %
B	5.5 %
acacia gum	0.5 %
glass	10 %

Example 8

only dry variant

tetrazene	25 %
penthrate	25 %
Fe ₂ O ₃	34 %
B	5.5 %
nitrocellulose	0.5 %
glass	10 %

Example 9

a) dry variant

tetrazene	25 %
penthrate	25 %
V ₂ O ₅	30 %
B	9.5 %
nitrocellulose	0.5 %
glass	10 %

b) wet variant

tetrazene	25 %
penthrate	25 %
V ₂ O ₅	30 %
B	9.5 %
acacia gum	0.5 %
glass	10 %

Example 10

a) dry variant

tetrazene	35 %
penthrate	15 %
SnO ₂	34 %
B	5.5 %
nitrocellulose	0.5 %
glass	10 %

b) wet variant

tetrazene	25 %
penthrate	25 %
SnO ₂	34 %
B	5.5 %
acacia gum	0.5 %
glass	10 %

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Example 11

a) dry variant

tetrazene	25 %
penthrite	25 %
MoO ₃	30 %
B	9.5 %
nitrocellulose	0.5 %
glass	10 %

b) wet variant

tetrazene	25 %
penthrite	25 %
MoO ₃	30 %
B	9.5 %
acacia gum	0.5 %
glass	10 %

Example 12

a) dry variant

tetrazene	25 %
penthrite	25 %
ZnO ₂	30 %
B	9.5 %
nitrocellulose	0.5 %
glass	10 %

b) wet variant

tetrazene	25 %
tetryle	25 %
ZnO ₂	30 %
B	9.5 %
polyvinyl alcohol	0.5 %
glass	10 %

Example 13

only dry variant

tetrazene	25 %
hexogene	25 %
CaO ₂	30 %
B	9.5 %
nitrocellulose	0.5 %
glass	10 %

Example 14

only dry variant – mixture with higher heating effect

tetrazene	25 %
penthrite	25 %
KNO ₃	33.5 %
B	6 %

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nitrocellulose	0.5 %
glass	10 %

Example 15

a) dry variant

tetrazene	35 %
penthrite	15 %
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$	31.5 %
B	8 %
nitrocellulose	0.5 %
glass	10 %

b) wet variant

tetrazene	25 %
hexogene	25 %
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$	31.5 %
B	8 %
acacia gum	0.5 %
glass	10 %

Example 16

a) dry variant

tetrazene	35 %
penthrite	15 %
$\text{Cu}(\text{NH}_3)_2(\text{NO}_3)_2$	27.5 %
B	12 %
nitrocellulose	0.5 %
glass	10 %

b) wet variant

tetrazene	25 %
hexogene	25 %
$\text{Cu}(\text{NH}_3)_2(\text{NO}_3)_2$	27.5 %
B	12 %
acacia gum	0.5 %
glass	10 %

Example 17 – with highly reactive oxidizing agent

a) dry variant

tetrazene	25 %
penthrite	25 %
BiO_2	33.5 %
B	6 %
nitrocellulose	0.5 %
glass	10 %

b) wet variant

tetrazene	25 %
hexogene	25 %
BiO_2	33.5 %
B	6 %
acacia gum	0.5 %
glass	10 %

Example 18 – analogous mixture

a) dry variant

tetrazene	25 %
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b) wet variant

tetrazene	25 %
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penthrite	25 %	tetryle	25 %
Bi ₂ O ₅	33 %	Bi ₂ O ₅	33 %
B	6.5 %	B	6.5 %
nitrocellulose	0.5 %	acacia gum	0.5 %
glass	10 %	glass	10 %

Example 19 – a specific case where oxidizing agent works as auxiliary explosive

a) dry variant

tetrazene	25 %
penthrite	25 %
Sn ₂ O(NO ₃) ₂	32 %
B	8 %
glass	10 %

b) wet variant

tetrazene	25 %
hexogene	25 %
Sn ₂ O(NO ₃) ₂	31.5 %
B	8 %
acacia gum	0.5 %
glass	10 %

Example 20

use of two oxidizing agents

tetrazene	30 %
penthrite	7.5 %
4BiONO ₃ (OH) ₂ .BiO(OH)	18 %
KNO ₃	17 %
B	5 %
nitrocellulose	0.5 %
glass	22 %

Industrial applicability

Mixtures that are in accordance with technical solution are utilizable in the field of ammunition production for the production of primers for central ignition cartridges intended for sports, hunting and practice purposes, or for shooting cartridges.

CLAIMS

1. A non-toxic and non-corrosive ignition mixture created by combining the energy system with the pyrotechnic system characterized by the fact that the mixture composed of the energy and pyrotechnic systems comprises 5 up to 40 weight percent of a high explosive, selected from the group of nitroesters and nitramines, 5 up to 40 weight percent of a sensibilizer, which is tetrazene or salts or derivatives of tetrazoles, 5 up to 50 % of an oxidizing agent selected from the group of oxides and peroxides of metals or from the group of salts of inorganic oxygen-containing acids or from the group of complex salts, 1 up to 20 weight percent of boron as a fuel, 5 up to 30 weight percent of a friction agent and optionally 0,1 up to 5 weight percent of a bonding agent.
2. The mixture according to claim 1 characterized by the fact that the high explosive is selected from the group of nitroesters such as penthrite, hexanitromannite, nitrocellulose, or from the group of nitramines such as hexogene, octogene, tetryle.
3. The mixture according to claim 1 characterized by the fact that the fuel is amorphous boron with specific surface of 5 up to 25 m²/g.
4. The mixture according to claim 1 characterized by the fact that the oxidizing agent is selected from the group of metal oxides such as oxides of copper, zinc, bismuth, iron, manganese, tin, vanadium and molybdenum, or from the group of metal peroxides such as peroxides of zinc and calcium, or from the group of salts of inorganic oxygen-containing acids such as saltpetre, basic nitrates of bismuth, tin and copper, or from the group of complex salts such as diammo-copper nitrate.
5. The mixture according to claim 1 characterized by the fact that the bonding agents are nitrocellulose, polyvinyl alcohol or acacia gum.

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6. The mixture according to claims 2 and 5 characterized by the fact that nitrocellulose applied in the organic solvent such as acetone functions, at the same time, as the bonding agent and energy component.
7. The mixture according to claim 1 characterized by the fact that the friction agent is ground glass.

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Non-toxic and non-corrosive ignition mixtureTechnical field

The invention concerns the field of ammunition production, especially the production of ignition mixtures for hunting and sports ammunition.

Background Art

All sorts of known ignition mixtures, which are presently used, i.e. both already dated mixtures based on mercuric fulminate, calcium chlorate and antimony sulphide, and newer non-corrosive mixtures based on tetrazene, lead trinitroresorcinate, lead dioxide, calcium silicide and antimony sulphide, emit during discharge a large amount of toxic heavy metals and they do not meet the environmental standards. That is why an extensive research has been carried out in the last ten years with an aim to develop a mixture that would not contain compounds of heavy metals such as lead, barium, mercury, antimony, and, at the same time, would retain non-corrosive properties of trisinate mixtures. The result is a mixture in which an aromatic diazo compound without metal content – dinol – fulfils the function of a primary explosive and tetrazene remains as a sensitizer. The pyrotechnic system is in this case composed of a new oxidizing agent, zinc peroxide and titanium powder. The mixture can contain also other components such as friction agents, typically ground glass, and active propellants such as various sorts of nitrocellulose and nitroglycerine powders.

Mixtures based on dinol are also known in which basically only the pyrotechnic system is modified. Oxidizing agents used include various oxides of metals – potassium nitrate, strontium nitrate, basic nitrates of copper and copper-ammonium nitrate and tin compounds. Neither these mixtures are a final solution. The basic problem here is the primary explosive itself – dinol. It is a carcinogenic compound with very unpleasant physiological effects. That is why there have been noted attempts to avoid dinol completely. EP 0656332 A1, in which the mixture is based only on pyrotechnic system and does not contain any explosive, offers one such solution. Here, the propellant is a hyperactive zircon powder, the oxidizing agent is a mixture of potassium nitrate and manganese dioxide, and the energy component is penthrite.

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CLAIMS

1. A non-toxic and non-corrosive ignition mixture created by combining the energy system with the pyrotechnic system characterized by the fact that the mixture composed of the energy and pyrotechnic systems comprises 5 up to 40 weight percent of a high explosive, selected from the group of nitroesters and nitramines, 5 up to 40 weight percent of a sensibilizer, which is tetrazene or salts or derivatives of tetrazoles, 5 up to 50 % of an oxidizing agent selected from the group of oxides and peroxides of metals or from the group of salts of inorganic oxygen-containing acids or from the group of complex salts, 1 up to 20 weight percent of boron as a fuel, 5 up to 30 weight percent of a friction agent and optionally 0,1 up to 5 weight percent of a bonding agent.
2. The mixture according to claim 1 characterized by the fact that the high explosive is selected from the group of nitroesters such as penthrite, hexanitromannite, nitrocellulose, or from the group of nitramines such as hexogene, octogene, tetryle.
3. The mixture according to claim 1 characterized by the fact that the fuel is amorphous boron with specific surface of 5 up to 25 m²/g.
4. The mixture according to claim 1 characterized by the fact that the oxidizing agent is selected from the group of metal oxides such as oxides of copper, zinc, bismuth, iron, manganese, tin, vanadium and molybdenum, or from the group of metal peroxides such as peroxides of zinc and calcium, or from the group of salts of inorganic oxygen-containing acids such as saltpetre, basic nitrates of bismuth, tin and copper, or from the group of complex salts such as diammo-copper nitrate.
5. The mixture according to claim 1 characterized by the fact that the bonding agents are nitrocellulose, polyvinyl alcohol or acacia gum.

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